Gas-phase reactions of tetraborane(10) with 1-en-3-ynes: syntheses of the parent tricarbahexaborane, *nido*-2,3,4-$C_3B_3H_7$, and its derivatives

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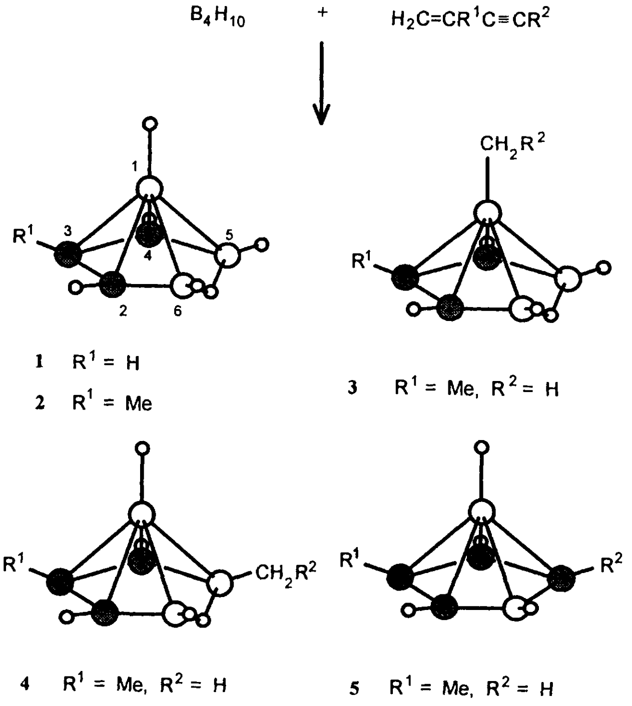
The gas-phase reaction at 70 °C between B_4H_{10} and 2-methylbut-1-en-3-yne, $H_2C{=}CMeC{\equiv}CH$, gives the new tricarbahexaborane derivatives 2–4 and the tetracarbahexaborane 5 as the major volatile products in an overall yield of 18%; reactions with $H_2C{=}CHC{\equiv}CH$ and $H_2C{=}CHC{\equiv}CMe$ lead to the first syntheses of the parent tricarbahexaborane *nido*-2,3,4-$C_3B_3H_7$ 1.

We have shown recently[1] that the mono-alkyl derivative 2-Me-2,3,4-$C_3B_3H_6$, reported by Bramlett and Grimes to be produced in 3% yield from the reaction of tetraborane(10) and ethyne at 50 °C,[2] is the only 2,3,4-tricarbahexaborane species to have been well characterised. Early, tentative reports of the synthesis of the parent compound, 2,3,4-$C_3B_3H_7$ **1**,[2–4] have since been discounted,[5,6] and compounds assigned[2] as the dimethyl derivatives 2,3- and 2,4-Me_2-2,3,4-$C_3B_3H_5$ and the trisubstituted compound 2-Et-3,4-Me_2-2,3-$C_2B_4H_5$, on the basis of NMR data available at that time, have been reidentified as the dicarbahexaboranes 2,4-Me_2-2,3-$C_2B_4H_6$, 5-Et-2,3-$C_2B_4H_7$ and 2-Et-3,4-Me_2-2,3-$C_2B_4H_5$, respectively.[1] A peralkylated species, 1,5,6-Et_3-2,3,4-Me_3-2,3,4-C_3B_3H, has been reported as a minor product from the dehalogenation of diethylboron chloride with lithium, but this has been identified by mass spectrometry only.[7] We now report a new synthetic route to 2,3,4-tricarbahexaboranes from gas-phase reactions of B_4H_{10} with the enynes $H_2C{=}CR^1C{\equiv}CR^2$ ($R^1 = R^2 = H$; $R^1 = H$, $R^2 = Me$; and $R^1 = Me$, $R^2 = H$). Some previously unknown di- and tetra-carbahexaborane derivatives are also produced in these reactions.

In a typical experiment, B_4H_{10} (0.5 mmol) and $H_2C{=}CMeC{\equiv}CH$ (1.5 mmol) were heated at 70 °C in a 1 litre Pyrex bulb with continuous mass-spectrometric monitoring of the gaseous reaction mixture. When the base peak from the enyne had disappeared (after *ca.* 30 min), the reaction was quenched by pumping the volatiles into a liquid-nitrogen-cooled trap. This process was repeated several times and the accumulated products were then fractionated on a cold column[8] with mass-spectrometric monitoring. Three volatile fractions were collected with cut-offs at *m/z* 90, 104 and 118. Accurate-mass measurements and high-field ^{11}B and ^1H NMR spectroscopy showed the *m/z* 90 fraction to contain 3-Me-2,3,4,5-$C_4B_2H_5$ **5**[9]† and the new tricarbahexaborane derivative 3-Me-2,3,4-$C_3B_3H_6$ **2**.‡ The second fraction (*m/z* 104) contained a mixture of 1,3-Me_2-2,3,4-$C_3B_3H_5$ **3**§ and 3,5-Me_2-2,3,4-$C_3B_3H_5$ **4**.¶ The least volatile fraction (*m/z* 118) consisted of a complex mixture of derivatives of the more familiar *nido*-dicarbahexaborane, 2,3-$C_2B_4H_8$; compounds identified include the mono-B-substituted derivative 2-Me-6-Et-2,3-$C_2B_4H_6$ and at least five di-B-substituted trimethyl derivatives, full details of which will be reported later. The approximate yields based on B_4H_{10} consumption for the volatile products **2**, **3**, **4** and **5** were 3, 4, 8 and 3% respectively, and the combined yield of the components of the third fraction was *ca.* 6%. The rest of the boron was incorporated into diborane, alkylboranes and involatile solids.

The tri- and tetra-carbahexaborane derivatives **2** and **5** are very similar in volatility, and emerge simultaneously from the cold column. However, they can be separated from one another by chemical means. Thus, **2** contains an acidic bridging hydrogen atom which can be removed by deprotonation with KH in diglyme to give the non-volatile solid K[3-Me-2,3,4-$C_3B_3H_5$], leaving **5** unaffected as a volatile liquid. The solid was exposed to DCl at −78 °C to give a bridge-deuteriated analogue of **2**. This procedure offers a route to the synthesis of pure **5** which should be superior to the reported method;[9] the latter involves the reaction of $MeC{\equiv}CH$ with 2,3-$C_2B_3H_7$ (10–20% yield from the reaction of B_4H_{10} and $HC{\equiv}CH$[10,11]), and results in a mixture in which 2-Me-2,3,4,5-$C_4B_2H_5$ is also present.

It is clear that the whole carbon backbone of the enyne is retained in the formation of **5**, whereas cleavage of the C≡C triple bond occurs in the formation of the tricarbahexaboranes **2**–**4** as shown in Scheme 1. This is apparent from the positions of the methyl groups attached to carbon in these compounds. The single CH group resulting from the cleavage of the enyne is not present in **2**, but does become incorporated into **3** and **4** as a methyl group attached to boron. These observations suggested that the reactions involving $H_2C{=}CHC{\equiv}CH$ and $H_2C{=}CHC{\equiv}CMe$ might yield *nido*-2,3,4-$C_3B_3H_7$ **1**, and this has been confirmed in both cases. The observed ^{11}B chemical shifts for this compound compare well with those predicted by the *ab initio*/IGLO/NMR method.[12]‖ The work is being extended to include reactions with other enynes, and the results and their mechanistic implications will be discussed more fully in a later report.



Scheme 1

The discovery of a new, potentially general, route to novel tri- and tetra-carbahexaboranes opens up the possibility of exploring the use of these species as ligands in the synthesis of novel metal complexes. The related pyramidal *nido* carbaborane ligand $[RR'C_2B_4H_4]^{2-}$ and the cyclic planar *arachno* system $[RR'C_2B_3H_5]^{2-}$, derived from it by removal of the apical BH unit, are all six-electron donors, isosteric and isoelectronic with the cyclopentadienide group,[13] and the same applies to monoanions of the 2,3,5-tricarbahexaborane system.[14] Such species are currently of great interest because of their ability to form stable complexes with metals, and to act as building blocks in the formation of multidecker sandwich systems.[15] Current research on these systems is also motivated by their potential use as alkene polymerisation catalysts and polymer precursors.[16]

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Footnotes

† *Spectroscopic data* for **5**: ^{11}B NMR ($CDCl_3$, 128 MHz, 223 K, *J*/Hz) δ 10.41 [d, 1 B, J_{BH_t} 147, B(6)], −57.0 [d, 1 B, J_{BH_t} 204, B(1)]; $^1H\{^{11}B\}$ NMR ($CDCl_3$, 400 MHz, 223 K) δ 5.67 [s, 1 H, C(4)H], 4.56 [s, 1 H, C(5)H], 4.48 [s, 1 H, C(2)H], 3.68 [s, 1 H, B(6)H], 2.30 (s, 3 H, Me), −0.70 [s, 1 H, B(1)H]. Accurate mass: *m*/*z* 90.0813. Calc. for $^{12}C_5{}^{11}B_2{}^1H_8$, 90.0813.

‡ *Spectroscopic data* for **2**: ^{11}B NMR ($CDCl_3$, 128 MHz, 223 K, *J*/Hz) δ 0.2 [dd, 2 B, J_{BH_t} 154, J_{BH_μ} 53, B(5), B(6)], −51.6 [d, 1 B, J_{BH_t} 193, B(1)]; $^1H\{^{11}B\}$ NMR ($CDCl_3$, 400 MHz, 223 K) δ 5.01 [s, 2 H, C(2)H, C(4)H], 3.41 [s, 2 H, B(5)H, B(6)H], 2.18 (s, 3 H, Me), −0.77 [s, 1, B(1)H], −3.76 (s, 1 H, H_μ). Accurate mass: *m*/*z* 90.0983. Calc. for $^{12}C_4{}^{11}B_3{}^1H_9$, 90.0983.

§ *Spectroscopic data* for **3**: ^{11}B NMR ($CDCl_3$, 128 MHz, 223 K, *J*/Hz) δ 0.9 [dd, 2 B, J_{BH_t} 153, J_{BH_μ} 47, B(5), B(6)], −43.1 [s, 1 B, B(1)]; $^1H\{^{11}B\}$ NMR ($CDCl_3$, 400 MHz, 223 K, *J*/Hz) δ 4.91 [s, 2 H, C(2)H, C(4)H], 3.45 [s, 2 H, B(5)H, B(6)H], 2.25 [s, 3 H, C(3)Me], −0.49 [s, 3 H, B(1)Me], −3.38 (s, 1 H, H_μ). Accurate mass: *m*/*z* 104.1139. Calc. for $^{12}C_5{}^{11}B_3{}^1H_{11}$, 104.1140.

¶ *Spectroscopic data* for **4**: ^{11}B NMR ($CDCl_3$, 128 MHz, 223 K, *J*/ Hz) δ 9.8 [d, 1 B, J_{BH_μ} 45, B(5)], −1.9 [dd, 1 B, J_{BH_t} 151, J_{BH_μ} 51, B(6)], −50.7 [d, 1 B, J_{BH_t} 187, B(1)]; $^1H\{^{11}B\}$ NMR ($CDCl_3$, 400 MHz, 223 K, *J*/Hz) δ 4.86 (s, 1 H, CH), 4.78 (s, 1 H, CH), 3.15 [s, 1 H, B(6)H], 2.23 [s, 3 H, C(3)Me], 0.48 [s, 3 H, B(5)Me], −0.75 [s, 1 H, B(1)], −3.25 (s, 1 H, H_μ). Accurate mass: *m*/*z* 104.1139. Calc. for $^{12}C_5{}^{11}B_3{}^1H_{11}$, 104.1140.

‖ *Spectroscopic data* for **1**: ^{11}B NMR ($CDCl_3$, 128 MHz, 223 K, *J*/Hz) δ 0.1 [d, 2 B, J_{BH_t} 155, J_{BH_μ} 70, B(5), B(6)], −55.2 [d, 1 B, J_{BH_t} 195, B(1)]; IGLO ^{11}B NMR δ −0.3 [B(5),B(6)], −57.9 [B(1)];[12] $^1H\{^{11}B\}$ NMR ($CDCl_3$, 400 MHz, 223 K, *J*/Hz) δ 7.05 [s, 1 H, C(3)H], 5.34 [s, 2 H, C(2)H, C(4)H], 3.50 [s, 2 H, B(5)H, B(6)H], −0.92 [s, 1 H, B(1)H], −3.83 (s, 1 H_μ).

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